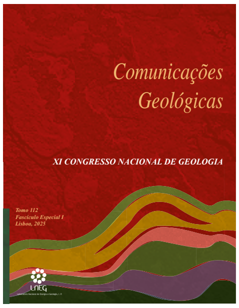
Comunicações
Geológicas

Comunicações Geológicas (2025) 112, Especial I, 253-256
ISSN: 0873-948X; **e-ISSN**: 1647-581X

Copiapite group: occurrence and properties in mining contamination scenarios

Grupo da Copiapite: ocorrência e propriedades em ambientes de contaminação mineira



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DOI: https://doi.org/10.34637/0fpt-qv44
Recebido em 30/09/2023 / Aceite em 15/01/2024

Artigo original
Original article

Abstract: The copiapite group shows a wide range of chemical compositions, allowing the identification of several mineral phases (e.g., aluminocopiapite and magnesiocopiapite). These minerals, typically observed in mining environments, are formed from evaporation and acid mine drainage (AMD) precipitation. In these areas, the copiapite has been studied to comprehend its ability to store some potentially toxic elements (PTE), specifically the As. Therefore, the present work aims to characterize mineral samples of copiapite using different techniques (binocular microscope, XRD, SEM-EDS, and FTIR) to understand their morphology, mineralogical and chemical composition, and environmental role. Copiapite samples were collected in two abandoned mining areas of the Iberian Pyrite Belt (IPB): São Domingos (Portugal) and Trimpancho (Spain). The results from the mining areas showed differences corresponding to two phases of the copiapite group, expressed by distinct occurrence modes and variations in morphology and chemical composition.

Keywords: Copiapite group, Acid Mine Drainage, morphology, chemical composition.

Resumo: O grupo da copiapite caracteriza-se por ter uma composição química variável, que se traduz na identificação de diferentes fases minerais tais como a aluminocopiapite ou a magnesiocopiapite. Este grupo, tipicamente observado em ambientes mineiros, forma-se através da precipitação e evaporação da drenagem **á**cida mineira e tem um papel fundamental na mobilização de elementos potencialmente tóxicos (EPT). Uma vez que tem a capacidade de reter estes elementos na sua composição, nomeadamente o As. Neste sentido, o presente trabalho tem como objetivo principal a caracterização mineralógica, morfológica e química da copiapite usando diferentes técnicas (microscópio binocular, XRD, SEM-EDS e FTIR). As amostras de copiapite foram colhidas em duas áreas mineiras abandonadas da Faixa Piritosa Ibérica (FPI): São Domingos (Portugal) e Trimpancho (Espanha). Os resultados mostram as diferenças entre amostras que representam duas fases deste grupo, evidenciadas quer por distintos modos de ocorrência, quer pelas variações na morfologia e composição química.

Palavras-chave: Grupo da copiapite, Drenagem Ácida Mineira, morfologia, composição química.

1. Introduction

The copiapite group has been described with a general formula of $MFe_4^{3+}[SO_4]_6(OH)_2\ 20H_2O$, where M= Fe^{2+}, $_{2/3}Fe^{3+}$, $_{2/3}Al^{3+}$, Mg, Ca, Zn, Cu (Ogorodova *et al*., 2021). This variety of chemical composition results in several types of copiapite: ferro-, calcio-, magnesio-, cupro-, alumino-, and zincocopiapite (IMA, 2023). Table 1 lists the copiapite group with the corresponding ideal formula. Copiapite minerals are frequently found in nature, especially in the oxidation zone of massive sulfide deposits, such as iron sulfide ores (Jamieson *et al*., 2005; Majzlan and Michallik, 2007). In mining environments, these secondary phases are observed as a product of the evaporation and precipitation of acid mine drainage (AMD) (Alpers *et al*., 2018; Paramanick *et al*., 2021). Copiapite triclinic minerals can occur as yellow to orange tabular crystals in aggregations or crusts (Jamieson *et al*., 2005) and are frequently associated with other secondary minerals such as melanterite, alunogen, fibroferrite, halotrichite, and other sulfates (Alpers *et al*., 2018).

A unique feature of these newly formed minerals is that they can incorporate potentially toxic elements (PTE), which change their geochemical cycling and, therefore, their behavior in the environment. Some studies explained this ability of secondary minerals through the attenuation and transport of PTE in mining areas affected by AMD (*e.g.*, Valente and Gomes 2009; Valente *et al*., 2013; Soyol-Erdene *et al*., 2018). However, slight changes in pH and Eh water conditions, promote the transformation to more stable phases (aging process), and climate conditions may result in the remobilization of different elements and acidity (Alpers *et al*., 2018; Soyol-Erdene *et al*., 2018). According to Nieva *et al*. (2021), copiapite is highly effective at temporarily sequestering arsenic (As) due to its high solubility but releases the metal back into solution during the wet season. This study aims to investigate naturally formed minerals of the copiapite group and improve our understanding of their geochemical cycling in mining degraded environmental systems.

Several techniques were used to characterize these materials, evaluate their role in retaining As, and understand their contribution to natural attenuation processes.

2. Study area

The selected study areas were São Domingos (Portugal) and Trimpancho (Spain) mining complexes (Figura 1), where the copiapite is a dominant secondary phase. Both abandoned mines belong to the Iberian Pyrite Belt (IPB), one of the largest sulfide mining provinces in the world (Grande *et al*., 2017). In general, the ore deposits are mainly

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Table 1. Minerals of the copiapite group.

Tabela 1. Minerais do grupo da copiapite.

Mineral	Ideal Formula
Copiapite	$Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Aluminocopiapite	$Al_{2/3}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Calciocopiapite	$CaFe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Cuprocopiapite	$Cu^{2+}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Ferricopiapite	$Fe^{3+}_{0.67}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Magnesiocopiapite	$MgFe^{3}_{+4}(SO_4)_6(OH_{)2} \cdot 20H_2O$
Zincocopiapite	$ZnFe^{3+}_4(SO_4)_6(OH)_2\ 20H_2O$

composed of pyrite (FeS_2), with lower contents of sphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), and other sulfides (Soyol-Erdene *et al*., 2018). This region has a historical past of intense mining exploitation, which resulted in large amounts of waste dumps and mining dams exposed to climate conditions. Therefore, the IPB is a unique region characterized by large contaminated and degraded areas caused by AMD processes (Grande *et al*., 2018).

São Domingos complex, in SE of Portugal, is one of the largest mines of IPB that was closed (in 1966) without environmental control until the rehabilitation process began in 2017. The area is characterized by red colored streams (São Domingos stream), efflorescent salts, ochre precipitates, and colloidal particles (Gomes *et al*., 2017 and 2022). In SW of Spain, the Trimpancho complex includes four medium-sized mines (Volta Falsa, Trimpancho Group, La Condesa, and Nuestra Señora del Carmen) that were closed several years ago without any rehabilitation process. The Trimpancho stream, which runs through the mining area, has been described as having high metal concentrations (Grande *et al*., 2018), and several AMD-precipitates have been identified (Soyol-Erdene *et al*., 2018). The two mining areas showed a typical pattern of AMD, with high acidity and contaminated waters discharged to the Chança Reservoir, built for human water supply.

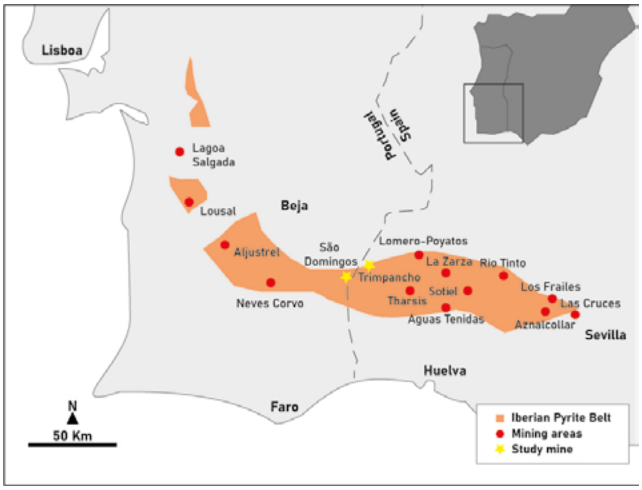

Figure 1. Geographical location of the study areas.

Figura 1. Localização geográfica das áreas de estudo.

3. Material and methods

Copiapite samples were collected in September of 2021 at the base of the waste dumps in both mining areas. Humidity and temperature were measured in the field using a portable thermo-hygrometer (HANNA digital Thermo-hygrometer HI9564, with probe HI 70602). The samples were stored in closed plastic vessels and transported to the laboratory from the Department of Earth Sciences, University of Minho (Portugal). Then, copiapite minerals were kept at temperature-controlled conditions (of 21ºC) without direct sunlight, avoiding any loss of water that can cause transformations into other mineral phases.

Binocular microscope, X-ray diffraction (XRD), Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), and Fourier-transform infrared spectroscopy (FTIR) were used to characterize minerals phases. The binocular microscope was used to visually screen the samples, allowing the differentiation of mineral phases and impurities. Mineralogical identification was obtained with a Philips PW1710 (APD-version 3.6 j) diffractometer, with CuKα radiation at 40 kV and 30 mA. XRD spectra were processed with the X'pert Pro-MPD software. Morphological and compositional features were analyzed by SEM-EDS using the VP SEM Hitachi S - 3400N. FTIR measurements of the samples were carried out using a PerkinElmer Spectrum Two spectrometer equipped with an ATR accessory. A diamond prism was used as the waveguide. All spectra were recorded with a resolution of 4 cm^{-1} in the wavelength region 4000-400 cm^{-1} by averaging 16 scans, and the analyses were carried out at room temperature.

To investigate the relationship between copiapite solubility, PTE mobilization and increased acidity in mining environments, 200 g of the Trimpancho sample was suspended in 50 mL of ultrapure water (from the Millipore System) in glass beakers at room temperature and agitated for 16 min with a magnetic stirrer. pH value was measured using a Thermo Scientific Orion 720A pH Meter. The As concentration in solution was determined according to the experimental method previously described by Lenoble et al. (2003).

4. Results and discussion

The copiapite mineral group occurs in the field with distinct colors and shapes: yellowish to greenish efflorescent coatings, scales, granular encrustations, or gel (Paramanick *et al*., 2021). These habits depend, in specific, on the relative humidity and temperature occurring in the mining area. In São Domingos, the copiapite formed a greenish gel layer covering the waste piles and acid lagoons banks. Trimpancho copiapite showed granular aggregates with a powdery yellow-green appearance at the base of the waste dumps. These morphological differences are shown in Figure 2.

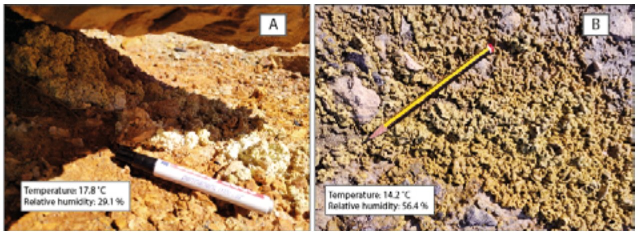

Figure 2. Different occurrences of copiapite: (A) yellowish granular encrustations, and (B) gel coatings.

Figura 2. Modos de ocorrência da copiapite: (A) agregados granulares de cor amarela, e (B) aspeto de gel.

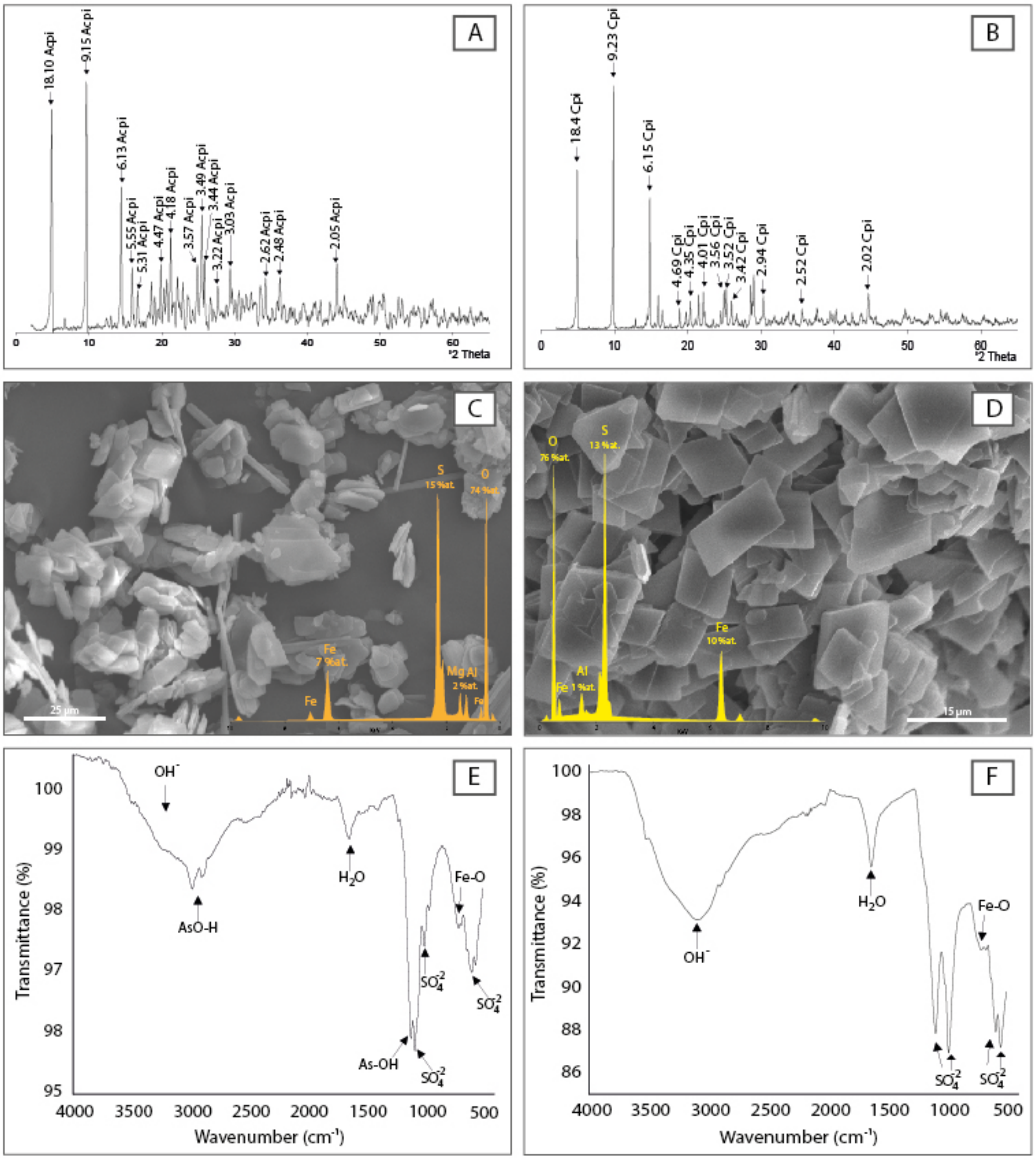

Figure 3. Results of the copiapite samples analyzed (aluminocopiapite (left) and copiapite (right)): (A-B) XRD pattern, (C-D) SEM images with the respective EDX spectra, and (E-F) FTIR spectra.

Figura 3. Resultados das amostras de copiapite analisadas (à esquerda aluminocopiapite e à direita copiapite): (A-B) padrão de DRX, (C-D) imagens de MEV com o espectro de EDX, and (E-F) espetros de FTIR.

The mineralogical composition of the studied salts was confirmed by XRD analysis, which revealed two different phases of the copiapite group (Figura 3 A and B). The Trimpancho sample shows a typical pattern of an aluminocopiapite, while the São Domingos sample was copiapite. The SEM images showed that both mineral phases have tabular shapes with minor variations (Figura 3 C and D). Aluminocopiapite appears with more rhombic aspect. The chemical composition obtained with SEM-EDX indicated slight differences between the Al concentration and the presence of Mg in the case of the aluminocopiapite.

Infrared transmission spectra for the two samples analyzed showed fingerprints of copiapite, as described by other authors (Majzlan and Michallik, 2007; Paramanick *et al*., 2021) (Figura 3 E and F). In the spectral region of 3600-2800 cm^{-1}, a broad band is assigned to the -OH stretching vibration of the structural hydroxyl groups and the presence of water (H_2O) molecules. A sharp band close to 1650 cm^{-1} corresponds to the $\delta(H_2O)$ vibration mode of the water. The strong band around 1070 cm^{-1} with a shoulder at 990 cm^{-1} is due to the symmetric stretching vibration mode of SO_4^{2-}. At lower wavenumber (small bands at 500 to 400 cm^{-1}) occurs the antisymmetric bending vibration modes of SO_4^{2-}. Finally, the weak bands between 700 and 800 cm^{-1} can be assigned to the Fe-O bending vibration. However, the aluminiocopiapite showed peaks at 2900-2800 cm^{-1} and 1117 cm^{-1} that correspond to the stretching region of AsO-H (Bullen *et al*., 2022).

A dissolution experiment was conducted to comprehend the potential impact of the As mobilization into the environment since the FTIR analysis indicated the presence of this element. Due to its high solubility, the mineral salt was quickly dissolved, and the pH solution changed abruptly from 4.7 to 2.23. The As concentration in the solution was around 1.5 µg g^{-1}.

5. Conclusions

São Domingos and Trimpancho mines were closed without environmental procedures, and the high amounts of waste continue to mobilize high levels of acidity, sulfates, metals, and metalloids. These leachates are discharged into the river network and are responsible for the watercourse's contamination. Therefore, the precipitation of secondary minerals has a vital role in the natural attenuation of contaminants.

The study focuses on the copiapite group, one of the dominant secondary phases for both mining areas. The samples collected showed two different phases of the copiapite group: aluminocopiapite and copiapite. These efflorescent salts had similar tabular shapes, with slight variation in the chemical composition compared to the typical chemical formula. However, the aluminocopiapite IR spectra showed the occurrence of AsO-H bands, illustrating the ability of this mineral to store some potentially toxic elements.

Therefore, the Trimpancho sample was submitted to a dissolution experiment to study and simulate the behavior of this mineral. This laboratory test showed the importance of aluminocopiapite in mining environments, particularly regarding the increase of acidity and As concentration during rainfall events.

Acknowledgments

Ana Barroso acknowledges FCT - Foundation for Science and Technology, I.P., by the support of ICT UID/QUI/0686/2020 through the research fellowship with reference UI/BD/151330/2021. FCT also co-funded this work through projects UIDB/04683/2020 and UIDP/04683/2020 and Nano-MINENV 029259 (PTDC/CTA-AMB/29259/2017).

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